N71-33692
NASA CR-121455

HEAT STERILIZABLE IMPACT RESISTANT CELL DEVELOPMENT

JET PROPULSION LABORATORY
CONTRACT 951296

REPORT FOR FOURTH QUARTER 1970

AND

FIRST QUARTER 1971

OCTOBER 1, 1970 TO MARCH 31, 1971

ESB INCORPORATED
EXIDE MISSILE AND ELECTRONICS DIVISION
RALEIGH, NORTH CAROLINA

APRIL 1971

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"This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics & Space Administration under Contract NAS7-100."

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APRIL 1971

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ABSTRACT, CONCLUSIONS AND RECOMMENDATIONS

Sixty sealed Ag-ZnO cells of 20 AH rated capacity were designed and manufactured to test the effect on cycle life of:

(1) Two regimes each one cycle per day at 50% depth of discharge -

Regime A - 20 2/3 hours charge/3 1/3 hours discharge

Regime B - 10 hours charge/14 hours discharge

(2) Wedge shaped vs standard negatives

(3) Extended vs standard negatives

(4) Two types of polypropylene absorbers and three GX wrap variations: positive, negative, and spiral wrap.

Initial cycles at 100% depth at 8 and 16 amperes predict maximum energy will be delivered by cell designs with extended or extended and wedge shaped negatives, positive wrapped cell packs containing Pellon 2140 and 8 layers GX or Kendall E1488 absorbers and 10L GX membrane. The same designs are superior on regime A and regime B cycling routines; however capacity loss during cycling is much greater on regime B -

Regime	Cycle	Range of Capacity Loss %/Cycle
A	20 2/3 hours C/3 1/3 hours D	0.2 - 0.5
B	10 hours C/14 hours D	0.9 - 2.2

Regime B is to be avoided if at all possible. Initial limiting currents and constant voltages must be selected for each cell design to assure charge input is equal to or slightly greater than the slow, efficient 14-hour discharge.

Erosion of the negative plate is the prime cause of failure on both regimes at the cycle life generated to date of 124 to 154 cycles.

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I. DEVELOPMENT OF HIGH CYCLE LIFE - 20 AH CELLS - TASK 10

A. Objectives and Past Work. - JPL Specification 50436-DSN-B and Modification 25 of Contract 951296 require development of a 20 AH sealed Ag-ZnO cell capable of 400 cycles at 50% depth of discharge. This cycle life is to follow a one-year prelaunch storage, heat sterilization for 72 hours at 135°C, flight acceptance tests, launch environments, 9-month interplanetary cruise and a soft landing impact of 200 g (0.7 msec).

A factorial experiment on 27 cells of 16 AH nominal capacity, having 9 layers of SWRI-GX membrane wrapped on negative plates, yielded one statistically significant variable. Capacity maintenance increased with increasing ZnO/Ag weight ratio at the test levels of 0.9, 1.2, and 1.5. Wet thickness of GX (2.0, 2.4, and 2.8 mils) and KOH concentration (41, 43, 45%) were not significant. After 100 cycles of 100% depth cells were dissected. Negative erosion was 50% or greater, top to bottom, leaving a dome shaped pattern in the lower 50% of plate area. Ag penetration increased with decreasing KOH concentration and increasing wet GX allowance (increasing KOH volume). Capacity fall off initially was greater than exponential and attributed to absence of a positive non-woven interseparator.

Sixty 20 AH cells were then manufactured to test on two cycle regimes, two positive non-woven polypropylene separators (Kendall E1488 irradiated and Pellon FT 2140), 8 vs 10 layers GX, extended vs non extended negatives, and three wrapping styles (positive, negative, and spiral).

All cells were heat sterilized wet sealed for 72 hours at 135°C. Weight loss was 0.5 to 1.5 g as water except for one cell which leaked at a metal plug - "O" ring - case seal. Cells were given three 100% depth cycles at discharge rates of 8, 3, and 16 amperes to 1.25 volts, then divided into two groups based on cycle regime.

B. Initial 100% Depth Cycles. - Mean cell attributes were calculated for the three initial cycles. Table I summarizes by design type discharge capacity, average voltage, and silver utilization for the eight and 16 ampere discharges to 1.25 volts, and the mean residual capacity in each cell group after the third cycle.

A possible ranking can be made of the initial cycling performance of the seven cell designs based on the assumptions that a desirable secondary energy package should have:

- high voltage and capacity
- equal charge-discharge capability at the 3 rates.

Cell Attribute		High ←		Ranking ← Design Type			← Low	
		-7	-6	-4	-5	-1	-2	-3
Absorber & Thickness								
Kendall	8		X	X		X	X	
	24							X
Pellon	11	X			X			
Layers GX	7							X
	8	X						
	10		X	X	X	X	X	
Wrap	+	X	X	X	X		X	X
	-					X		
Spiral								X
Negative	Wedge		X					
	Std.	X		X	X	X	X	X
Extended Negatives		X	X	X	X			X
Capacity Out								
	8A	3	2	3	4	1	5	6
	16A	3	1	5	2	7	6	4
Voltage on Load								
	8A	1	5	2	4	3	6	7
	16A	1	5	4	2	3	6	7
Residual Capacity After 3rd Cycle		1	2	3	6	6	4	5
Rank Score		9	15	17	18	20	27	29
Rank		1	2	3	4	5	6	7

High ranking cells have extended negatives and positive wraps.

C. Regime A 20 2/3-Hour Charge/3 1/3-Hour Discharge Cycling. - After the initial cycle tests were completed, the cells were divided into two groups for 50% depth cycling on regime A (20 2/3-hour charge/3 1/3 hour discharge) or regime B (10-hour charge/14 hour discharge. Table II gives assignments and cycles to date. Figure 1 gives the decay of end-of-discharge voltage (last voltage recorded during discharge time) as a function of regime A cycles completed for each cell design. Figure 2 gives typical complete charge-discharge curves for three of the best cell designs at cycles 10 and 132. . Cell designs 1 and 2, and possibly 3, have reached the point of capacity limitation by one cell of the group. Cell designs 1 and 2 both have non-extended negative plates and 10L GX membrane. Cell design 3 has 7L GX and 6L non-woven polypropylene in a spiral positive wrap. The lower voltages of the spiral wrap throughout cycling is consistent with the loaded voltages for this cell design in Table I for cycles 1 and 3 at 8A and 16A respectively. To compensate for the higher internal resistance of design 3 the charge voltage was revised from 1.95 volts per cell to 1.96 volts per cell at cycle 135. Designs 4, 5, 6, and 7 continue to cycle satisfactorily at 125 cycles. No prediction can be made at this point concerning meeting the cycle life goal of 400 50% depth cycles.

D. Regime B 10-Hour Charge/14-Hour Discharge Cycling. - Twenty-five cells - 5 each of cell designs 1, 2, 5, 6, and 7 were placed on regime B modified constant voltage auto-cycling at 50% depth of rated capacity. Table II gives cycles completed to date. In this orbit the discharge rate is very low and efficient and the charge rate is higher and less efficient. During the first 10 cycles the initial limiting charge current was raised from 1.05 amperes to 1.15 amperes, increasing charge acceptance in the 10-hour period to equal discharge output. At cycle 28 integrations of charge and discharge curves showed output was still exceeding input for some of the cell designs. The cycling constant charge voltage was then increased from 1.95 to 1.96 volts per cell. Table III gives the increases in end of discharge voltages resulting - dramatic in cell designs 2 and 5. Only cell design 7 failed to show an increase in voltage.

Approximately 60 cycles later a second increase in voltage of 0.01 volts to 1.97 volts per cell was implemented to benefit cell design 2 primarily. Figure 3 shows the benefit was short-lived in cell design 2 and just perceptible in cell designs 5 and 6. Shortly thereafter one cell of five in the design 2 battery failed to deliver 10 ampere-hours even when charged at 1.97 volts per cell. Group 2 is therefore considered a failed group on the regime B test. The failing cell (S/N 19) was dissected and found to have negative plates eroded from top to bottom more than 50%. A single positive plate from this cell delivered after recharge 81% of the original cycle 2 output. Thus after 107 regime B cycles capacity losses for cell type 2 plates were estimated to be:

- positives 19% max.
- negatives 50% max.

Based on cycling data developed on regime B to date the best four cell designs ranked in order of highest sustained voltage to lowest are designs 6, 7, and 5.

E. Residual Capacity Measuring Cycles. - At intervals of approximately 50 cycles on the automatic cycling regimes each 5-cell group was charged by extending the charge time until the charge current decayed to 0.2 ampere at the constant charge voltage. Each cell was then discharged at the 8 ampere rate to 1.25 volts, and the capacity thus delivered was assumed to be the residual capacity in the cell. On regime A (20 2/3 hour charge/ 3 1/3-hour discharge) the cycle charge time normally increased to 25 hours before the charge current decayed to the cut-off. On regime B (10-hour charge/14 hour discharge) charge time was approximately doubled. Figure 4 is a summary of the capacity decay from cycle 3 to cycle 106 for each cell design. The major response is the test regime. Regime B cells - all five designs - decreased in capacity 50% at rates from 0.9 to 2.2% per cycle, while regime A cells decayed at rates from a maximum 0.5% to 0.2% per cycle.

Ranking of the cell designs under test according to best capacity maintenance gives:

Regime A - Designs 7, 4, 6, 5, 3, 1, 2

Regime B - Designs 6, 7, 5, 1, 2

Qualitatively the poorer cell design will perform less effectively on both regimes. Qualitatively also the performance on initial 100% depth cycles 1 and 3 predicted the better cycling cell designs before cycling was initiated. See Section B and Table I.

F. Cell Electrolyte Leakage. - Electrolyte leakage has been observed as carbonate mossing around pressure gage seals and terminals. Table IV summarizes leakage sites found to date and the calculated seal reliability. In no case has the electrolyte loss by weight measurements exceeded the weight loss as water diffusing through the case during heat sterilization for 72 hours at 135°C. Eliminating the pressure gage to cover leakage the reliability after 4 months of cycling is 0.916 with 3 leaks on positive and 2 leaks on negative terminals in 60 cells.

One mechanism for leakage revealed by cell dissection is the development of fine cracks radiating out from terminal holes in the molded PPO 534 - 801 covers after extended heat sterilization in nitrogen at 135°C. For these parts the Skydrol 500A residual stress test showed marginal stress in the covers as received from the molder. See Figure 5. Parts machined from Alpha-Lux (PPO 534-801) 1/2-inch thick sheet exhibited satisfactory stress. As the radial cracks develop cell electrolyte can bypass the "O" ring epoxy seals. Improved molding techniques or covers machined from PPO 534-801 slab stock are solutions to this problem.

II. QUALITY ASSURANCE

Quality assurance engineers monitored the 72 hour heat sterilization of 60 cells at 135 ±3°C in pure nitrogen: 10 cells each in cell designs 1, 2, 5, 6 and 7 and 5 cells each in cell designs 3 and 4. Two cells (S/N 48 and 49) leaked through cracks in the molded cover radiating out from terminal holes. Weight loss as electrolyte and water was 18.5 and 8.6 grams for cells S/N 48 and 49 respectively while non-leakers lost weight as water in the range 0.5 to 1.5 grams. Design 6 cells were reduced by the failures of S/N 48 and 49 from 10 to 8 and were cycled as two groups of four rather than five each. Failure analyses were performed on S/N 48 and 49 up to identification of leakage mechanism.

Residual stress tests as described in Section I-F were performed to identify the degree of stress locked into the covers during the molding cycle, and solutions to the problem were recommended.

One cell of design group 2 (S/N 19) was dissected after a capacity failure on regime B residual capacity test. A detailed failure analysis report was prepared and submitted to JPL. Cause of failure was negative plate erosion after 107 cycles.

III. FUTURE WORK

Cycling of the 20 AH cells and failure analyses of failing cells will continue to the end of the negotiated contract work period - August 31, 1971. The estimated number of 50% depth cycles completed by surviving cells on that date is 250 - 275 cycles on both regimes A and B. Cells not dissected will be handled as directed by JPL.

TABLE I

MEAN 20 AH CELL DISCHARGE PERFORMANCE ON
100% DEPTH INITIAL CYCLES

Absorber Type	Absorber Wet Thickness Mils	Capacity (AH), Voltage (Volts), Efficiency (AH/gAg), and Residual Capacity — Extended (E) vs Non-Extended Negatives (NE), Number Layers GX, Wrap Type: 7L + E	8L + E	10L + NE	10L + E	10L + E and Wedge	10L — NE	RATE Amp	CODE
Kendall E-1488	8			(-2) (6)	(-4) (3)	(-6) (2)	(-1) (5)		
				26.1	26.6	26.8	27.1	8	C
				1.418	1.444	1.423	1.436		V
				0.366	0.374	0.377	0.381		E
4 mil each layer				22.7	23.0	24.6	22.6	16	C
				1.350	1.371	1.360	1.376		V
				0.319	0.323	0.346	0.318		E
				3.3	2.7	0.5	5.1		RC
	24	(-3) (7) Spiral Wrap							
		25.9						8	C
		1.410							V
		0.363							E
		23.6						16	C
		1.339							V
		0.333							E
		3.7							RC
Pellon 2140 one layer	11		(-7) (1)		(-5) (4)				
			26.6		26.5			8	C
			1.458		1.433				V
			0.374		0.363				E
			24.2		24.3			16	C
			1.407		1.378				V
			0.340		0.342				E
			-0.2		5.1				RC

Note: Design No. ( ) ( ) Performance Rank

TABLE II

50% DEPTH AUTO-CYCLES AND TEST PARAMETERS

Test Parameter or Cell Design Type	Unit	Cycles Completed* Regime A	Regime B	Cycles at Failure
Design Type 1	ea.	135	154	
2	"	128	146 (2F)	107 123
3	"	134	NT	
4	"	124	NT	
5	"	131	145	
6	"	133	154	
7	"	133	149	
Charge Time	Hrs.	20.67	10.0	
Voltage	V/C	1.95	1.95	
Current	Amps	0.50	1.15	
(Limiting Value)				
Discharge Time	Hrs.	3.33	14.0	

(*) Each cycle as a 5-cell battery.

2F - Two cells failed of five.

TABLE III

INCREASE IN END-OF-DISCHARGE VOLTAGES WITH INCREASE IN CHARGE VOLTAGE ON REGIME B
(10-HOUR CHARGE/14-HOUR DISCHARGE)

Design Group	Last Cycle	Charge Voltage Before Increase	Charge Voltage After Increase	End-Of-Discharge Voltage Before Increase	End-Of-Discharge Voltage After Increase	End-Of-Discharge Voltage Change
A. First Adjustment						
2	32	1.95	1.96	1.23	1.54	+ .31
5	50	1.95	1.96	1.47	1.55	+ .08
1	50	1.95	1.96	1.50	1.56	+ .06
6	50	1.95	1.96	1.53	1.56	+ .03
7	38	1.95	1.96	1.55	1.55	0
B. Second Adjustment						
2	86	1.96	1.97	1.48	1.50	+ .02
5	97	1.96	1.97	1.52	1.53	+ .01
1	95	1.96	1.97	1.53	1.53	0
6	97	1.96	1.97	1.53	1.54	+ .01
7	85	1.96	1.97	1.53	1.53	0

TABLE IV

ELECTROLYTE LEAKAGE ON 20 AH CELLS DURING CYCLING

Leakage Site	Cycle Regime	Number of Leaks 11/25/70 - 3/31/71	Total No. Cells	Reliability
Around gage to cover seal or plug to cover seal	A	3	36	
	B	2	24	
	Total	5	60	.917
Positive Terminal	A	1	36	
	B	2	24	
	Total	3	60	.950
Negative Terminal	A	2	36	
	B	0	24	
	Total	2	60	.966
Total No. Leaks Observed		10	60	.834

NOTE: Electrolyte leakage is determined by visual observation of carbonate formation at the leak site.

FIGURE 1

REGIME A END OF DISCHARGE VOLTAGES ON 50% DEPTH CYCLING TEST
20 AH CELLS

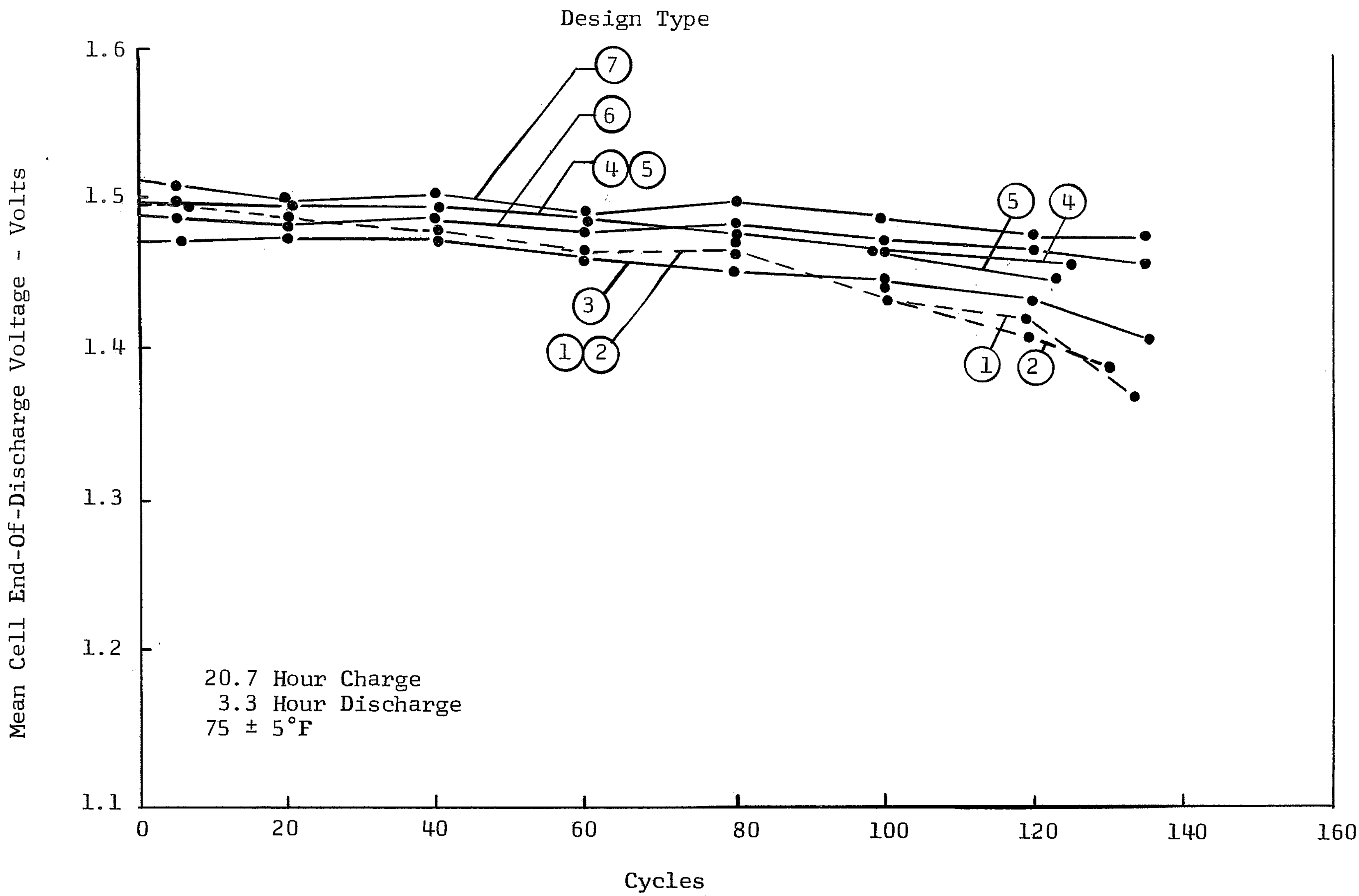


FIGURE 2

TYPICAL CELL VOLTAGE DURING REGIME A CYCLE
DESIGN 5

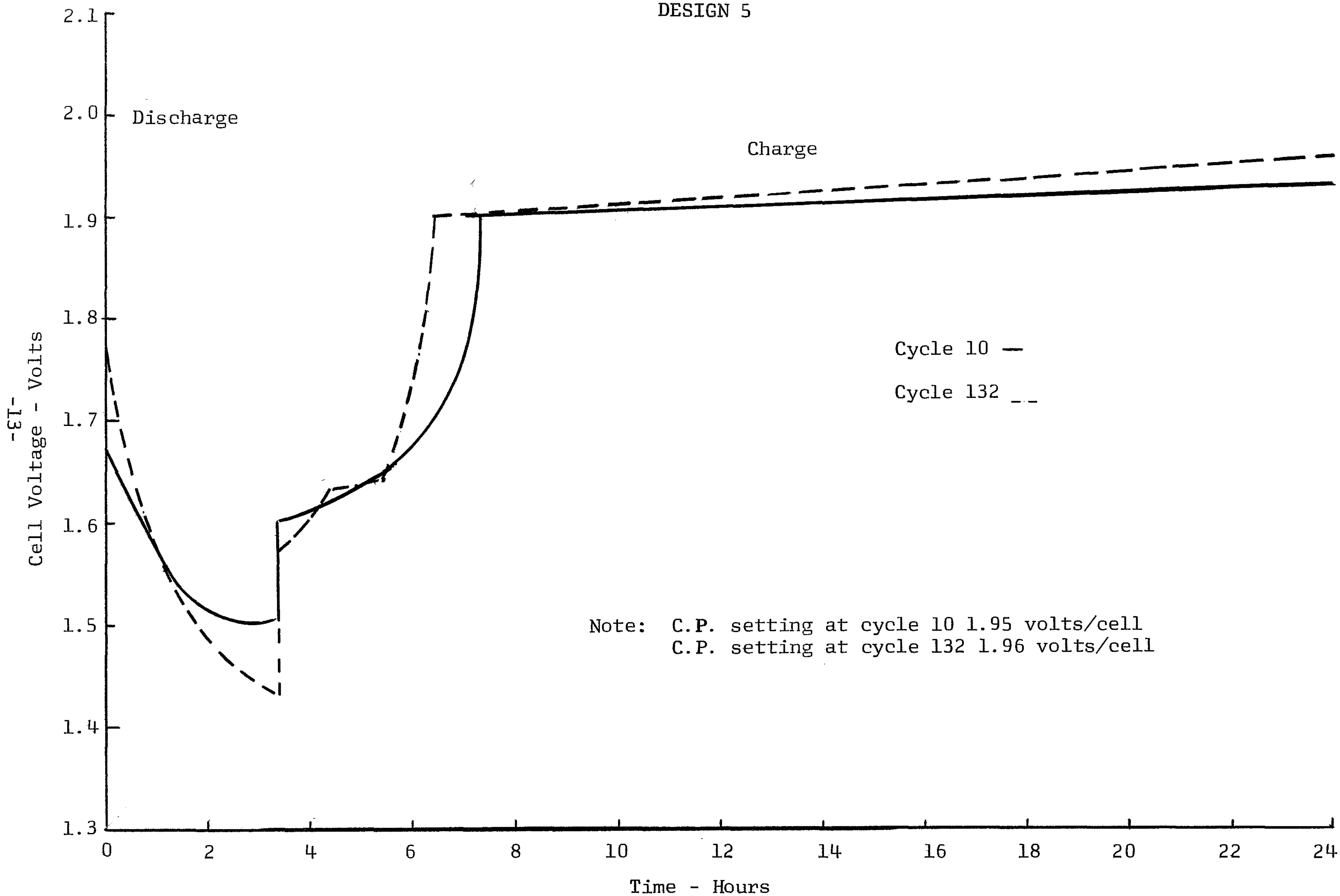


FIGURE 2A

TYPICAL CELL VOLTAGE DURING REGIME A CYCLE - DESIGN 6

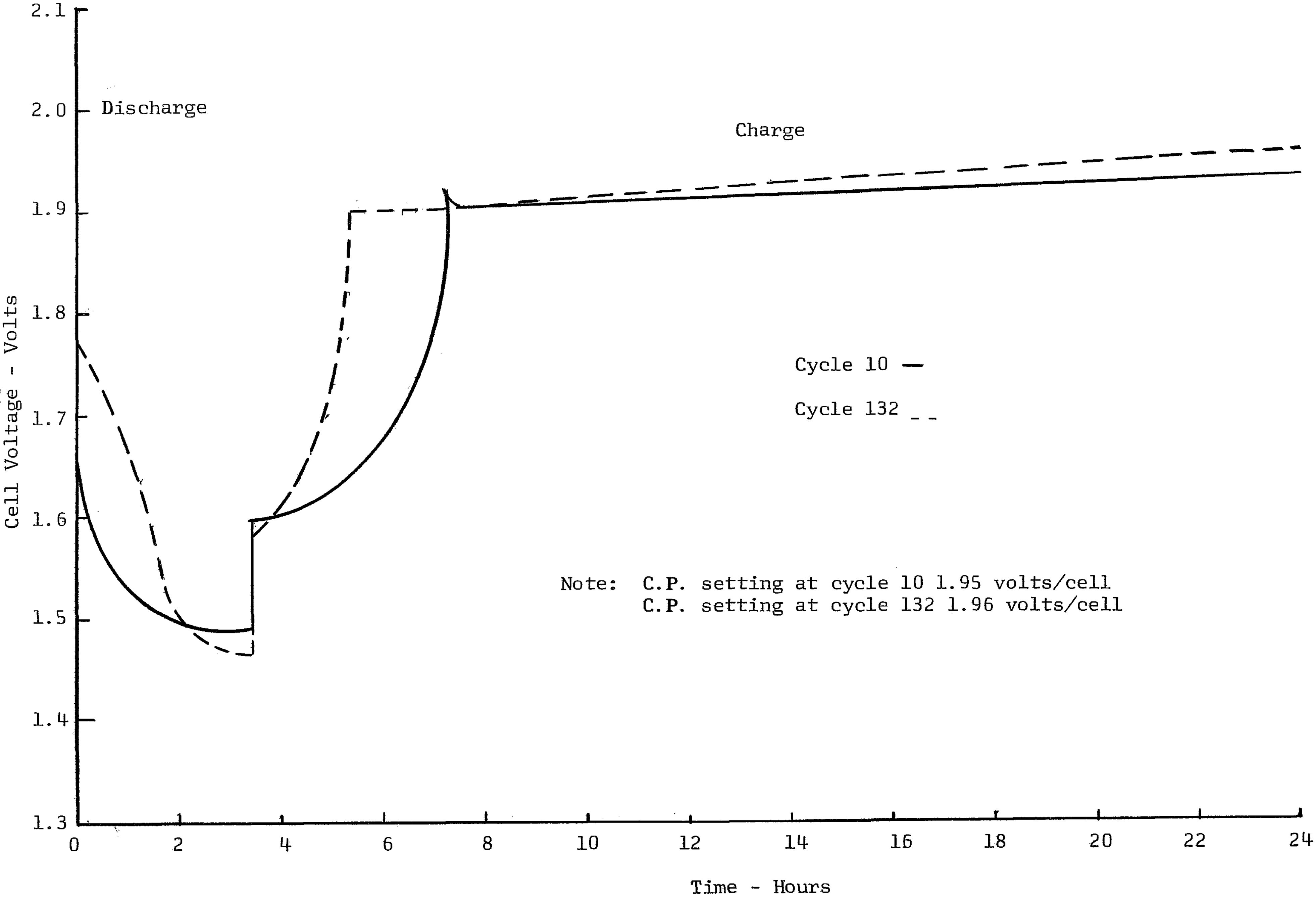


FIGURE 2B

TYPICAL CELL VOLTAGE DURING REGIME A CYCLE - DESIGN 7

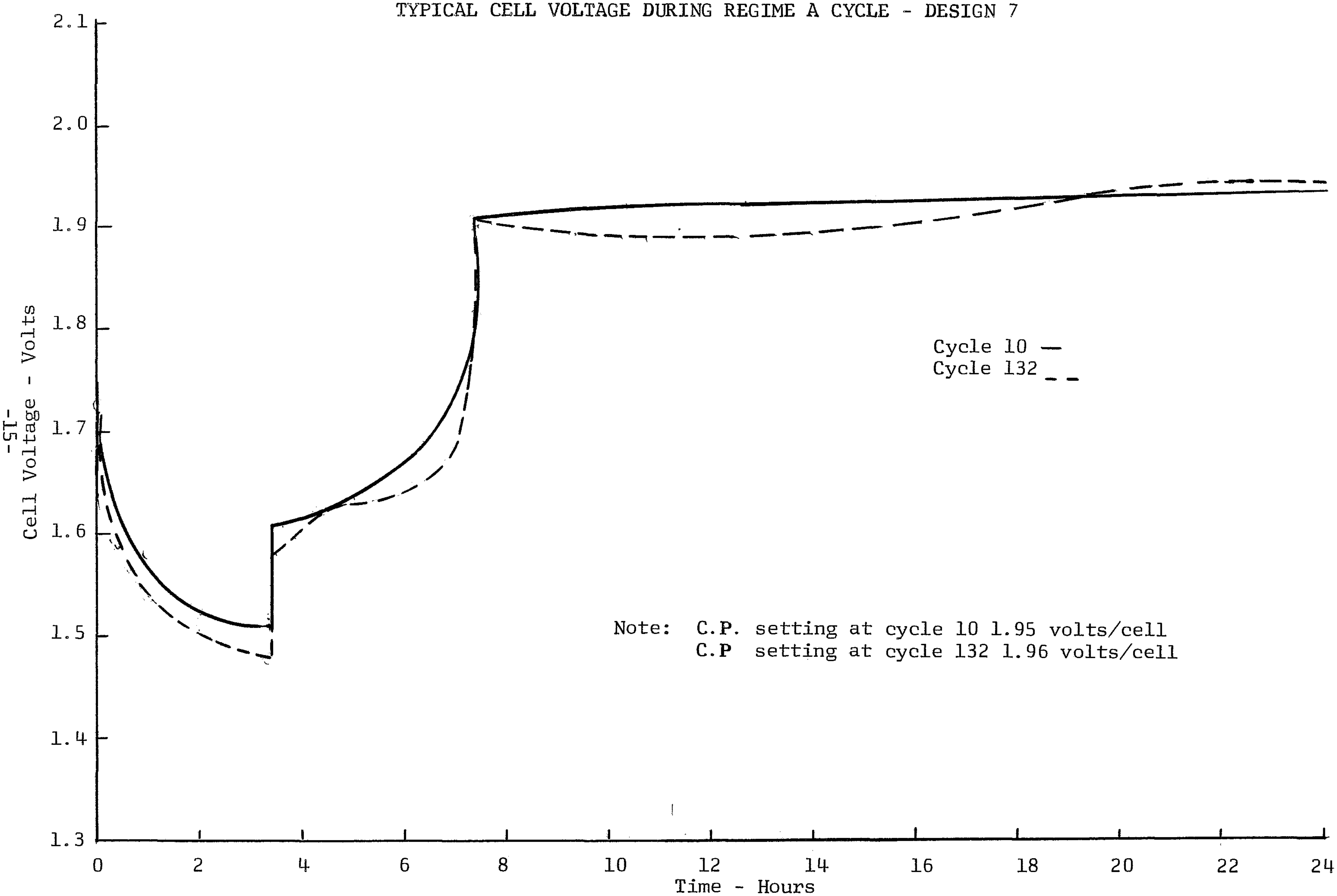


FIGURE 3

END OF DISCHARGE VOLTAGE
10-HOUR CHARGE/14 HOUR DISCHARGE
50% DEPTH
20 AH CELLS
75 ±5°F

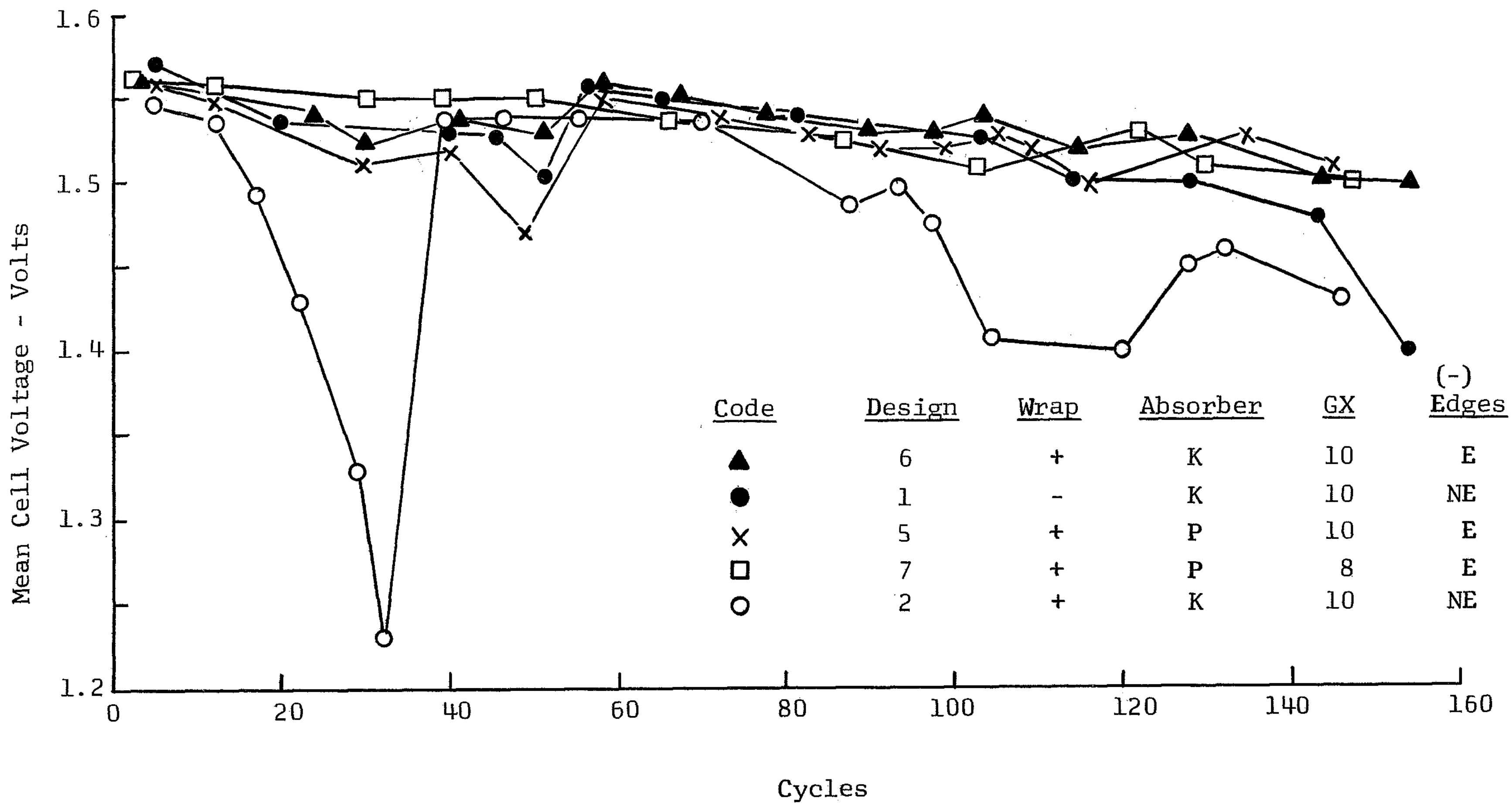


FIGURE 4

100% DEPTH CAPACITY DURING 50% DEPTH AUTOCYCLING

Design and Orbit	Plates Wrapped	Extended Negatives	Negative Shape	Separator System
1A & 1B	Neg.	No	Flat	10L SWRI-GX 2L EM476I
2A & 2B	Pos.	No	Flat	10L SWRI-GX 2L EM476I
3	Pos.	Yes	Flat	7L SWRI-GX 6L EM476I Spiral Wrap
4	Pos.	Yes	Flat	10L SWRI-GX 2L EM476I
5A & 5B	Pos.	Yes	Flat	10L SWRI-GX 1L Pellon 2140
6A & 6B	Pos.	Yes	Wedge	10L SWRI-GX 2L EM476I
7A & 7B	Pos.	Yes	Flat	8L SWRI-GX 1L Pellon 2140

A = Orbit 20 2/3 hours charge, 3 1/3 hours discharge.
B = Orbit 10 hours charge, 14 hours discharge.

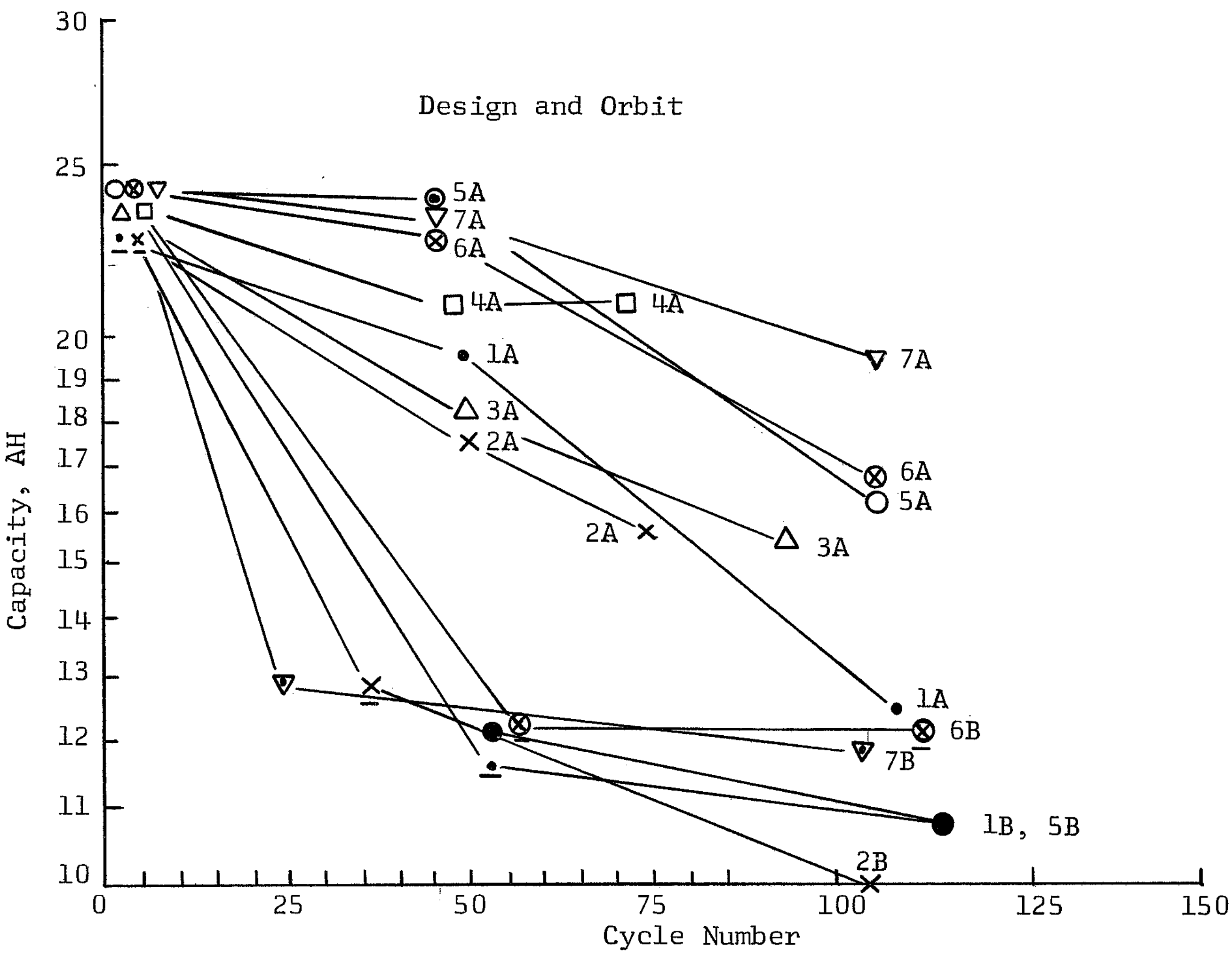
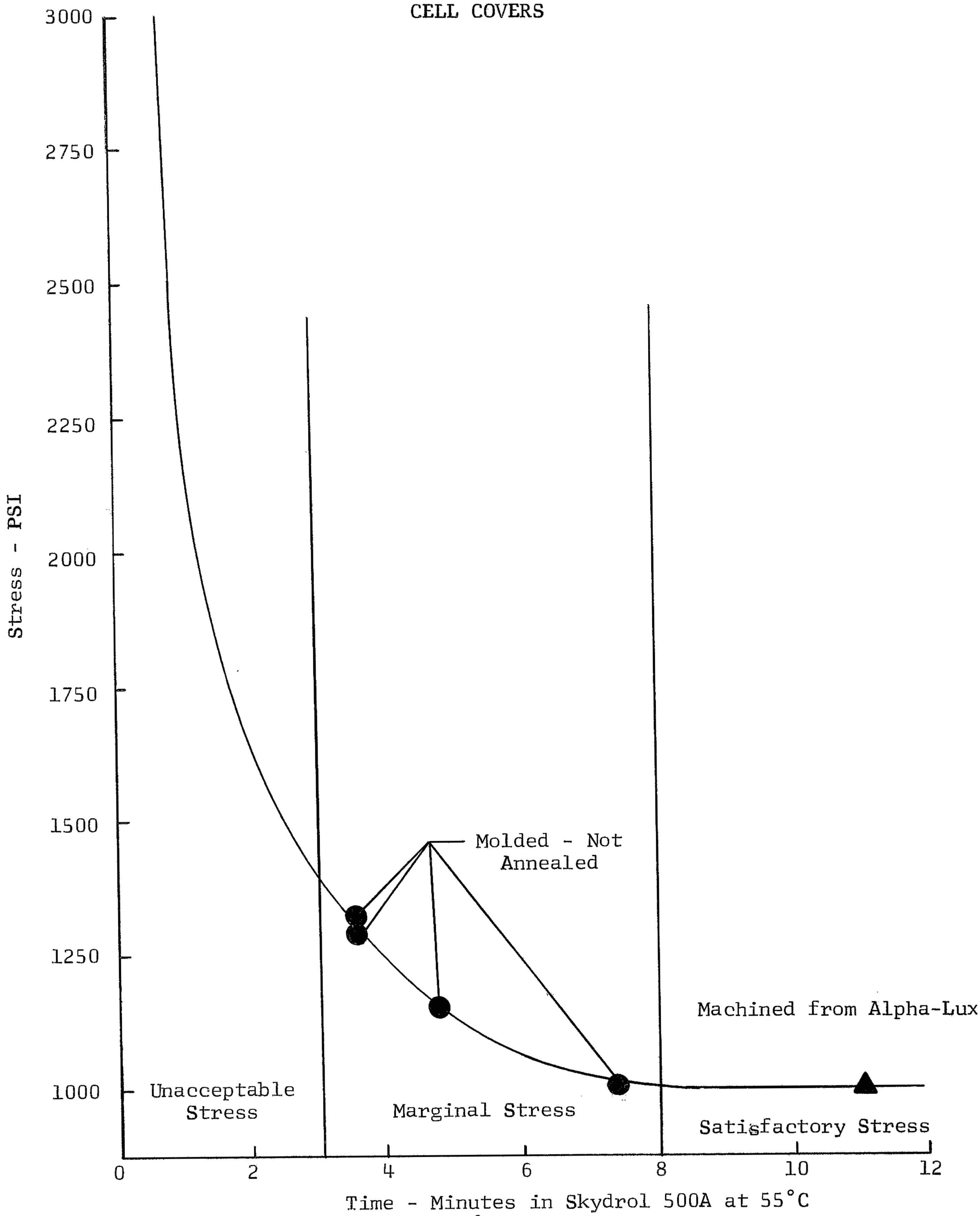


FIGURE 5

SKYDROL 500A
RESIDUAL STRESS
TEST ON
CELL COVERS



Note: Time to crack for PPO in 55°C bath.